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## SCANNING ELECTRON MICROSCOPY OF HIGH SPEED FIBER IMPACT PHENOMENA

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### SYNOPSIS

Visual observation of nylon impacted at very high speeds, including ballistic speeds, shows a large amount of plastic deformation and melting of the broken fiber ends. In attempts to produce fibers for special applications, manufacturers have produced organic fibers with moduli greater than that of glass, and with heat resistance values far greater than that of nylon. The initial products of this type showed a typically brittle fracture, because of their low ductility. They also showed a tendency to split longitudinally. The better products show this splitting to a more marked degree, to where it reaches a state best described as fibrillation. This process is thought to be of considerable importance, because (a) it tends to minimize premature brittle fracture, and (b) considerable energy is absorbed in creation of the many subsurfaces.

The potential for high strength in these new aromatic polymers is probably due to the extended polymer chains, which are broken more nearly in unison during extension. However, the realization of these high strengths with such low elongation fibers depends upon the process of fibrillation, to prevent premature catastrophic failure. The strength of the aromatic polyamide "Fiber B" is 23 g/d or 400,000 psi, as contrasted to 10 g/d or 150,000 psi for the strongest nylon tire cord previously available. The theoretical value of approximately 200 g/d or 4,000,000 psi can be calculated on the basis of all primary bonds breaking at once.

### INTRODUCTION

The effect of high-speed impact upon fibrous materials has been the subject of numerous papers in the last forty years. A monograph by Lyons summarizes a good deal of that work [1]. The major objectives were: (a) to investigate the fundamental viscoelastic properties of polymeric fibrous materials, and (b) to predict the performance of fibrous materials under field conditions by laboratory procedures. Many devices were used in an attempt to simulate field conditions, such as the action of cords in auto and truck tires, the opening of a military parachute, high speed stitching, and ballistic impact. The devices included relatively low constant speed testers, such as the Instron, falling weight devices in which the testing speed is governed by the drop height, pendulums, rotating disk machines, pneumatic testers, and actual transverse impact in which a missile strikes a yarn perpendicular to the long fiber axis. The testing speeds covered the range from fractions of a millimeter per second to a thousand meters per second. The transverse impact test can be varied to include most velocities encountered in the field of ballistic protection, where the fibrous materials may

be destined for use in a vest, to provide protection against pistol fire or fragmenting munitions. These studies led to an understanding of the significant rate dependence exhibited by fibrous materials. The general trends of increasing breaking strength, modulus, and decreasing elongation at break with increasing rate of testing has been documented [1-6]. Many of these publications relate this behavior to the concept of relaxation times and/or the ability of molecular groupings to move in a given time frame [3-5].

A dramatic example of the inability of an important process to take place in a short testing time is furnished by undrawn nylon. This material possesses a huge capacity for work absorption when tested in tension at slow speeds in an Instron. Attempts to capitalize upon this property by using undrawn nylon for a ballistic vest have failed [1]. Obviously the process of drawing cannot occur in the time frame of interest in ballistic impact. This behavior of undrawn nylon has been shown more clearly with transverse impact experiments on yarns [7]. The researchers took a series of nylon 66 yarns, which differed systematically in mechanical properties, and subjected these yarns to static rates of straining as well as to ballistic rates of straining. The undrawn nylon specimens absorbed 260 J/g in a slow tensile test of 1.67%/sec, because of its large elongation at that rate of testing. However, they absorbed only 10 J/g under transverse impact at a high speed of 5000%/sec. More highly drawn yards exhibited a much more modest loss in breaking energy with an increase in straining rate. The study showed that an undrawn nylon should not be an effective energy absorber at the high rates of loading characteristic of those encountered in aerial delivery. Additional tests with undrawn nylon at even higher rates of loading confirmed experimentally the poor performance demonstrated in a ballistic vest.

In any failure process study it is useful to investigate the morphology of the material after fracture. Earlier, any investigation of fracture surfaces was necessarily limited to that possible with light microscopy, and later with the transmission electron microscope. In 1958 an extensive microscopic study was conducted of a multilayer nylon armor panel upon transverse impact with .22 caliber missiles, but the study was restricted to the use of light microscopy [8]. Some valuable information was obtained concerning the fusion of nylon fibers and the extreme localization of the effect of the impact. The information was obtained with difficulty through painstaking and tedious work, due to the small depth of focus attained in light microscopy.

Now, with the advent of the scanning electron microscope (SEM), it is possible to investigate more efficiently the morphology of fibrous materials degraded by high speed impact. Such a study has been conducted and is the subject of this paper. The materials considered have included not only nylon but also the new, high modulus aromatic polyamides.

## EXPERIMENTAL

### Tensile Tests

Tensile data were generated at two rates of straining, a conventional textile testing rate of 1.67%/sec, and the fastest rate available with a pneumatic tester,

5000%/sec. The latter rate of testing is still short of that characteristic of ballistic impacts, but it is the highest rate of testing for which transducers can give an accurate measure of load and deflection. This limitation is mainly due to wave effects.

The conventional tests were performed with a standard Instron Tensile Tester, operating at a constant extension rate of 2.1 mm/sec. The high speed tests were performed on the FRITS\* Piston Tester, which is pneumatically driven by compressed nitrogen gas at approximately 6.42 m/sec. All tests at both strain rates were performed on specimen lengths of 128 mm (5 in.), with a pretension of approximately 12 g applied immediately before clamping. The specimens were individually weighted after test to establish the denier (linear density) in each case.

### Scanning Electron Micrographs

The broken ends of the fractured yarns were mounted on specimen studs with silver paint and single-faced adhesive aluminum tape. The samples were coated in a vacuum evaporator at  $3 \times 10^{-5}$  torr with a thin layer of carbon, followed by a thin layer of gold. The carbon deposition allows better distribution of the subsequent gold coating. During the coating process the samples were rotated  $360^\circ$  and tilted  $180^\circ$  to obtain a uniform and complete coating. The fracture patterns of the coated samples were observed in an AMR Model 900 scanning electron microscope in the secondary electron mode.

## RESULTS AND DISCUSSION

Scanning electron micrographs have greatly facilitated the investigation of fiber morphology after high-speed impact. The depth of focus available with the SEM makes it possible to observe many fibers at once. For example, Figure 1 shows fractured ends of nylon fibers resulting from impact with a small, 10 caliber cylinder, weighing 87 mg. Fusion is clearly indicated from the mushroom-like appearance at the end of almost every broken fiber. Although ballistic impact has been emphasized, it should be pointed out that such fusion and mushroom shaped ends have also been observed in fibers after longitudinal impact at only 30 m/sec, as well as in ballistic impact [8, 9].

In order to develop fibrous materials with a greater potential for high performance in industrial and military applications, such as tire cords, parachute suspension lines, and ballistic protective items, it is necessary to take into account one or more of the following factors: (a) Improved mechanical properties of yarns, especially strength, generally yield better candidates in fabric form for defeating fragments, whereas decreased creep can eliminate flat-spotting in tires; (b) raising the melting point and strength retention at high

\*Fabric Research Impact Test System.

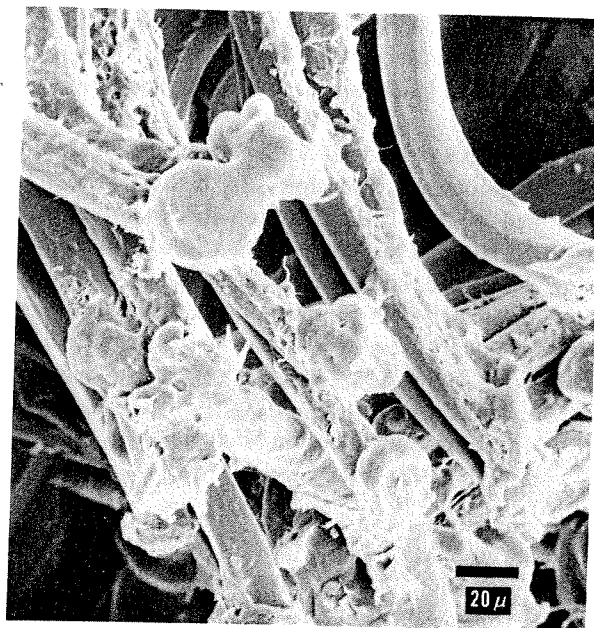


FIG. 1. Nylon fibers broken and fused from missile impact; 450X.

temperature of a fiber may yield better candidates for resistance to high speed impact; (c) a higher modulus to density ratio (specific modulus) would increase the fiber's ability to respond quickly to high speed impact, so that it would mitigate the extreme localization of the deformation previously noted by Susich [8].

The first of these factors, improvement in the mechanical properties of nylon 6 and nylon 66, has been studied by tire cord manufacturers. The results have been fairly negative, as the changes in molecular weight necessary to produce stronger fibers makes the polymers impossible to spin on a production basis. This is due to the fact that the intrinsic viscosity rises very fast with molecular weight, and the polymers are intractable, although they have super-strength potential [10, 11].

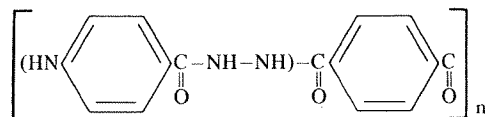
The second and third objectives, higher heat resistance and faster response to impact, could be addressed by the introduction of aromatic groups in the polymer backbone. It has been shown that both modulus and melting point could be raised significantly by the introduction of benzene rings in the main chain [12]. Properties of many aromatic and aromatic-aliphatic polyamides tend to verify this contention [13]. Poly (p-phenylene adipamide), the product of adipyl chloride and paraphenylene diamine, has a melting point of 340°C, as contrasted with the 255°C value characteristic of nylon 66, which has the same acid unit but is made with an aliphatic amine component [13, 14]. Polyterephthalamides, made by interfacial polymerization, exhibit generally high

melting points. For example, the product of tetramethylene diamine and terephthaloyl chloride, has a melting point of 436°C [15].

This rise in melting point when compared to nylon, is of course partially due to the reduction in the number of methylene groups in the diamine, but the major influence of the phenyl groups is apparent. This influence can be demonstrated with atomic models by contrasting the flexibility of polyethylene with that of either poly(p-phenylene) or the aromatic-aliphatic polymers described here. The stiffness of the aromatic polymers results in a lower change in entropy from the solid to the liquid, because of the restrictions in the number of configurations possible, as compared to an aliphatic polymer. The melting point of a material is inversely proportional to the entropy change upon melting, and must necessarily rise with increased stiffness.

Modulus is also related to stiffness. Poly(tetramethylene terephthalamide) exhibits a modulus of over 90 g/d or 1,500,000 psi, as contrasted with 40 g/d or 580,000 psi for all aliphatic nylon 66 [15]. A fairer comparison with nylon 66 would be the polymer prepared from hexamethylene diamine and terephthaloyl chloride, which has a modulus 50% greater than the aliphatic nylon. In any event, the potential for the preparation of fibers with increased heat resistance and larger moduli by the introduction of aromatic groups has been demonstrated clearly some years ago. Problems arise in the preparation of large quantities of these polymers and in the conversion of them into fibers. Only two processes were available for preparation, namely interfacial polymerization and low temperature solution polycondensation. The former method yields a product from diacid chloride and diamine, which is never really in solution. Then a method of spinning the fiber has to be found. Even the aliphatic-aromatic polyamides, such as polyhexamethylene terephthalate cannot be melted without decomposition. An all aromatic polymer would be even more likely to decompose upon melting. Even solution spinning, a less desirable process, is difficult, because of the insolubility of these aromatic polymers. Solvents such as concentrated sulfuric acid are generally required, which are not convenient for large scale production. These difficulties have in the past restricted the fiber preparation to laboratory quantities.

The first appearance of aromatic polyamide fibers in more substantial quantities was a family of fibers produced by Monsanto and designated as X-500. These fibers are reported to have an aromatic polyamide-hydrazide structure:



Black et al. have discussed these fibers in some detail [16, 17]. The X-500 yarns are quite temperature resistant with little weight loss up to 400°C. The temperature resistance is also obvious from the absence of fused fibers after ballistic impact, as shown in Figures 2 and 3. These micrographs also indicate the

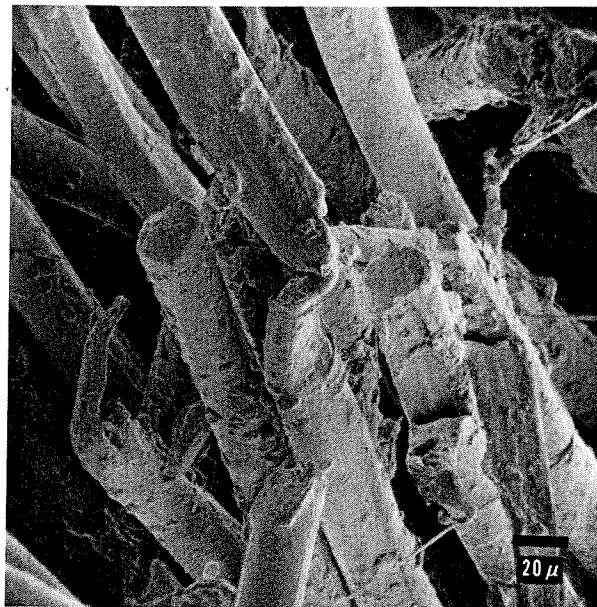


FIG. 2. X-500 fibers broken from ballistic impact; 400X.

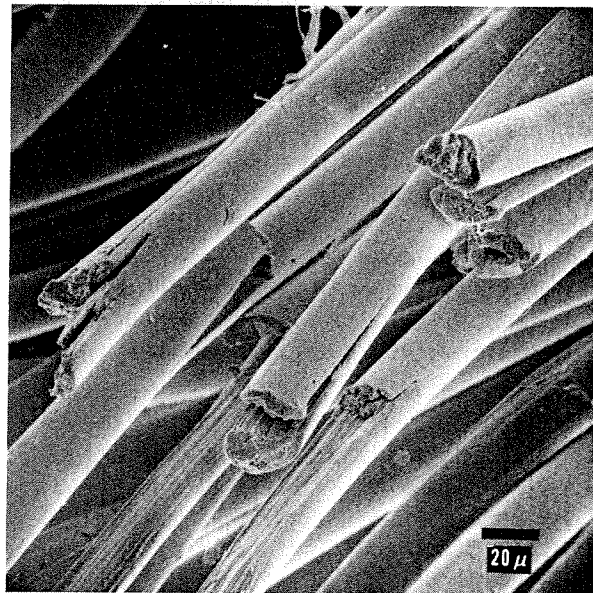
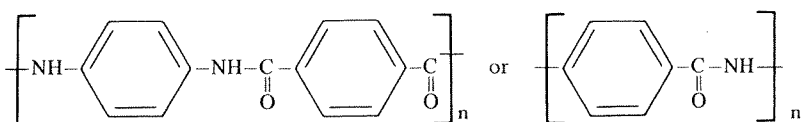


FIG. 3. X-500 fibers have the tendency to split longitudinally from impact; 410X.

predominance of brittle fracture, which might have been predicted from the stress-strain properties of the X-500 type yarns. These properties are compared in Figure 4 with those of nylon 66. The yarns were tested both at a static (1.67%/sec) and a dynamic (5000%/sec) rate of straining. The increased modulus is quite apparent from the curves, which also show the rather modest strength and work to rupture. One of the reasons for these modest strength values may be the intensional break-up of the order through the introduction of comonomers.

A more successful product has been marketed by DuPont under the designations PRD 49-IV and Fiber B. This material is reported [17, 18] to have a structure like:



The first structure is analogous to nylon 66, whereas the second is similar to the repeat structure of nylon 6. This all-para aromatic polyamide possesses a strength of 23 g/d at slow rates of straining. The properties of Fiber B at slow strain rate of 1.67%/sec are given in Table I in units familiar to either engineers, textile technologists, or physical scientists. It is interesting to compare these values with those for nylon and other conventional fibers. The sound velocity value of 9400 m/sec is higher than the 2400-3400 m/sec for nylon or even the 4800-6000 m/sec for steel. This high value is due to the high modulus value, which is approximately equal to that of glass on a psi scale but vastly superior on a specific modulus or textile basis. It has been shown that moduli in the range of  $10^{12}$  dyn/cm<sup>2</sup> can be estimated for poly(1,4 benzamide) and poly(1,4 phenylene terephthalamide) [18]. The calculations are based upon values for the force constants of the chemical bonds in the polymer chain as derived from vibration frequencies.

The strength values exhibited by PRD 49-IV are the highest exhibited by any fibrous material. They can be compared with the 10 g/d value of nylon tire cord, the strongest fiber cord used commercially. A simple calculation can be made to

TABLE I

Mechanical Properties of Fiber B at Strain Rate of 1.67%/sec			
Property	English Units	Textile Units	Metric Units
Strength	430,000 psi	23 g/d	$2.9 \times 10^{10}$ dyn/cm <sup>2</sup>
Modulus	11,000,000 psi	600 g/d	$7.7 \times 10^{11}$ dyn/cm <sup>2</sup>
Elongation	3.7%	3.7%	3.7%
Sound Velocity	31,300 ft/sec	—	9400 m/sec

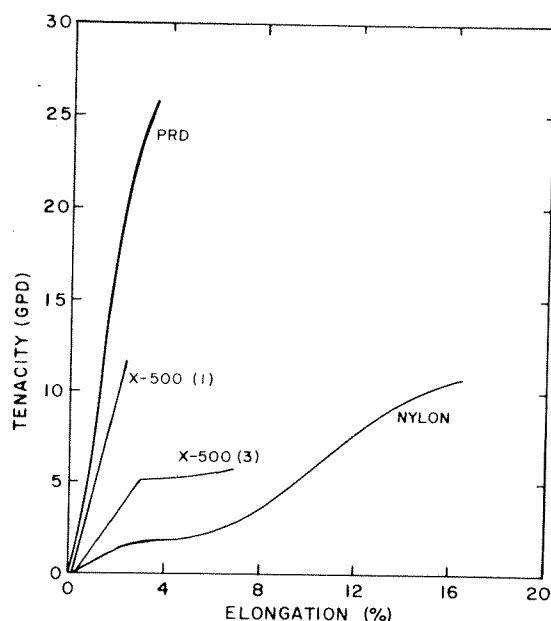


FIG. 4. Tensile stress-strain properties of new high modulus fibers at a strain rate of 5000%/sec.

estimate the theoretical strength possible in an organic polymer such as Fiber B. For this purpose the following assumptions have to be made: (a) bond breaking predominates; (b) the lowest bond energy involved is that of a C-C single bond,  $5.5 \times 10^{-12}$  erg/bond or 80 kcal/molecule; (c) the effective distance for force application is 0.2 Å; (d) the cross-section occupied by each polymer molecule is a square 10 Å by 10 Å. Based upon the above assumptions, the force involved in breaking each molecular chain would be  $2.8 \times 10^{-3}$  dyn. The theoretical strength can then be calculated from the product of the individual chain strength and the  $10^{14}$  chains that can fit in 1 cm<sup>2</sup> cross-section. This product of  $2.8 \times 10^{11}$  dyn/cm<sup>2</sup> is equivalent to  $4.1 \times 10^6$  psi in English units. For conversion to the unusual units used in the textile industry, it is necessary to introduce a density value of 1.45 g/cm<sup>3</sup>. The figure thus obtained, 220 g/d, is almost 10 times that found for Fiber B. One conclusion from this comparison is that the 23 g/d achieved may only be the beginning for further improvements. Values of 30 to 40 g/d may be possible by breaking a larger fraction of molecules simultaneously. On the other hand, it is not likely that the theoretical value can be reached, since that requires that 100% of the chains break simultaneously. Even the observed strength of 23 g/d requires that over 10% of the chains break simultaneously. Because chain folding appears to be the rule in crystalline morphology, simultaneous breaking of many molecular chains does not occur.

It is proposed that the structure of the new aromatic polyamide polymers favors extended chains, in which simultaneous rupture is more likely than for



folded chains. Lindenmeyer has discussed chain folding in some detail, and has indicated some of the factors favoring this phenomenon. These factors include: (a) a single molecular weight species making up the material, (b) low molecular weight, (c) high temperature and pressure [19]. Actually, Lindenmeyer points out that folded chains are not favored energetically, because energy is needed to insert a crystalline fold. However, the energy required is more than compensated for by the decrease in energy resulting from the molecular portions brought into crystalline register. The ability for the extended chains to be brought into crystalline register is probably the real key to the behavior of the new polymers.

The previous discussion of properties is somewhat speculative, and it is useful to return to the SEM in an attempt to determine the morphological characteristics of the fractured PRD fibers. Figure 5 shows a single fiber from a yarn after tensile impact failure at 5000%/sec. Fiber B is much smaller in diameter than usual for industrial fibers. For example, Fiber B is less than  $11.7\text{ }\mu\text{m}$ , whereas nylon tire cord fibers are over  $27\text{ }\mu\text{m}$ . The microfibers produced by the tensile test, as shown in Figure 5, are approximately  $1\text{ }\mu\text{m}$  in diameter. This fiber break-up can possibly be related to the high strength observed. The longitudinal splitting of the fibers nullifies the more conventional process, in which failure is propagated perpendicular to the fiber axis. This tendency to split rather than melt has been seen earlier with X-500 aromatic type fibers (Fig. 3), but the amount and degree of splitting was less pronounced [20]. Fibrillation of Fiber B is not limited to impact speeds. In Figure 6, Fiber B yarn fractured at a relatively slow tensile rate of straining at 1.67%/sec shows the same fibrillation, and the fibrils are again less than  $1\text{ }\mu\text{m}$  in diameter.

The new high modulus fibers, such as X-500, PRD 49-III, and PRD 49-IV (Fiber B), were actually developed for applications in tire cord and laminates, where superior strength and modulus properties could produce longer wearing tires without flat spotting and composite structures with high strength and stiffness to weight ratios [21]. A laminate was prepared from Fiber B fabric and

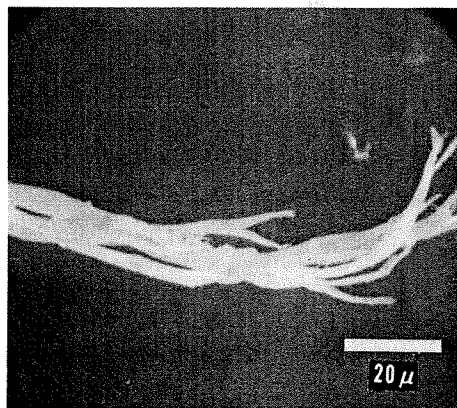


FIG. 5. Fibrillated appearance of PRD 49-IV fiber after tensile impact at 5000%/sec; 650X.

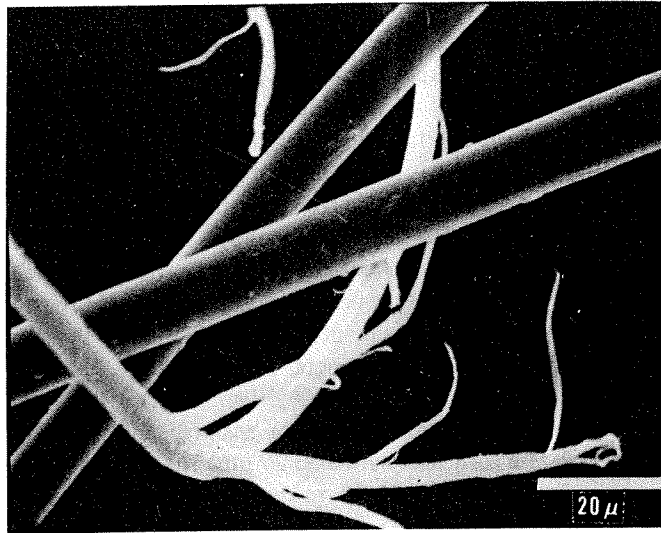


FIG. 6. Fibrillated fiber of PRD 49-IV after slow-speed test; 800X.

phenolic-modified polyvinyl butyral resin. The resulting laminate was impacted transversely with .22 caliber fragments of the type used by Susich [8]. A great deal of fibrillation was noted in the vicinity of the missile hole, as shown in Figure 7. Although changes were made in the structure, type of straining, and rate of impact, a similar type of fibrillation is observed in Figure 7 as had been shown in Figures 5 and 6.

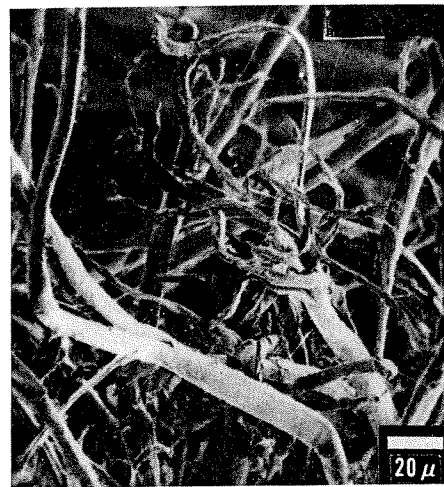


FIG. 7. Composite form of PRD 49-IV after impact with .22 Caliber missile; 360X.

## SUMMARY

It has been shown that new organic fibers are now available with moduli as high as glass. The most successful to these, the PRD-49-type fiber developed by DuPont is probably based upon an all-para condensation product of p-phenylene diamine and terephthalic acid. The strengths exhibited, 20-25 g/d, are double those previously available commercially. SEM micrographs of the fractured fiber ends show that fibrillation appears to be characteristic, regardless of testing speed, type of impact, or lamination. The superior properties of PRD 49-IV fiber are probably due to (a) extended chain-tie molecules, (b) a nearly perfect crystalline register, and (c) crack blunting through fibrillation.

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